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(57) Abstract:

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CONSTITUTION: A slurry composed mainly of terephthalic aid and ethylene glycol is supplied to a reaction zone to effect continuous esterification reaction. In this process, the slurry density is measured by placing a liquid densitometer in a channel to supply the slurry to the reaction zone to continuously detect the molar ratio of ethylene glycol to terephthalic acid in the slurry and the esterification reaction is controlled based on the detected molar ratio.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the approach of esterifying a terephthalic acid and ethylene glycol.
[0002]
[Description of the Prior Art] As the industrial manufacture approach of polyethylene terephthalate, a terephthalic acid (henceforth "TPA") and ethylene glycol (henceforth "EG") are esterified directly, screw (beta-hydroxyethyl) terephthalate and/or its low-grade polymer (henceforth "BHET") are obtained, and the direct polymerization method which carries out the polycondensation of this further is adopted widely in recent years.
[0003] In order to obtain the product polymer of high quality in this direct polymerization method, it is important to fully control the rate of esterification of BHET. Although it is possible as a method of controlling an esterification reaction to make regularity the mole ratio of TPA and EG of a raw material, it is usually difficult to carry out measuring supply of the fine-particles-like TPA with high degree of accuracy, and usually hard to remove 1 - 3% of error.
[0004] Moreover, although esterification conversion can be searched for by sampling a reactant and measuring the acid number and saponification value, it is difficult for it for delay to produce in correspondence only the time amount which about [that it cannot respond to automation of a process by the approach of analyzing by such help] or analysis takes, and to maintain conversion uniformly. Then, the approach of measuring the refractive index of gaseous-phase gas all **** of for example, a reaction band or the electrical conductivity of reactant gas, and controlling an esterification reaction as an approach for solving this problem, is proposed (JP,55-79349,A, JP,60-104125,A).
[0005]
[Problem(s) to be Solved by the Invention] However, a reaction was not necessarily able to be completely controlled by the limitation of the effect resulting from the terms and conditions of the system of reaction, and device measuring precision only in the combination of the above-mentioned approach.
[0006]
[Means for Solving the Problem] Then, paying attention to correlation with the mole ratio of TPA and EG in the slurry which uses as a principal component TPA and EG which are supplied to an esterification reaction zone region, and a slurry consistency, by measuring a slurry consistency, this invention person etc. found out that it was possible to control an esterification reaction, and reached this invention.
[0007] That is, by making it face the summary of this invention to supply the slurry which uses TPA and EG as a principal component to a reaction band, and to esterify continuously, installing a liquid density meter in the slurry supply way to a reaction band, and measuring a slurry consistency, the mole ratio of EG to TPA in a slurry is detected continuously, and it consists in the continuation esterification approach of the terephthalic acid characterized by controlling an esterification reaction based on this mole ratio.
[0008] This invention is explained to a detail below. The slurry which usually becomes the reaction vessel in which BHET exists from TPA and EG as the approach of esterification in this invention is supplied continuously, and a multistage successive reaction tub and the approach of making it

esterify continuously using two steps of reaction vessels preferably are usually used. Although components other than the residue of TPA and EG could be contained in part in BHET and BHET was obtained by the approach of well-known arbitration, it is desirable to use as it is what was obtained by said approach.
[0009] the mole ratio of EG/TPA of the slurry which consists of TPA and EG -- usually -- 1.2-2.0 -- it is preferably desirable 1.4-1.8, and to be referred to as 1.5-1.7 the optimal. Other glycol components other than EG(s), such as dicarboxylic acid components other than TPA, for example, isophthalic acid, 5-sodium sulfoisophtharate, adipic-acid, sebacic-acid, naphthalene dicarboxylic acid, and diphenylsulfone dicarboxylic acid, for example, tetramethylene glycol, neopentyl glycol, 1, and 4-cyclohexane dimethanol etc. exceeds and twists 30-mol % to a part, and may usually be contained in this slurry the grade at it.
[0010] An esterification reaction is usually the gage pressure of 0.5kg/cm2, in order to control diethylene-glycol (henceforth "DEG") concentration. It is 0.15kg/cm2 preferably hereafter. It carries out below. Moreover, 230-260 degrees C of temperature of an esterification reaction are 220-270 degrees C usually 240-260 degrees C the optimal preferably. If an esterification reaction does not advance substantially at less than 220 degrees C but it exceeds 270 degrees C on the other hand, DEG concentration increases [neither of] and it is desirable.
[0011] 90% or more, although it is 94 - 96% the optimal, when changing the conversion of obtained BHET, the polycondensation reaction rate in a polycondensation process is changed, and preferably, 90 to 98%, since the quality of the polyester obtained varies, the conversion of BHET supplied to the polycondensation process which is degree process usually becomes indispensable [stabilizing and manufacturing BHET with fixed esterification conversion obtaining the polyester of high quality].
[0012] In this invention, it has the description on the occasion of the above esterification at the point which installs a liquid density meter in the slurry supply way to a reaction band, and measures a slurry consistency on-line. The EG/TPA mole ratio in a slurry consistency and a slurry has a correlation, for example, a related Fig. like drawing 1 is obtained. Then, by measuring a slurry consistency, continuous detection of the EG/TPA mole ratio is carried out, and it becomes possible to control an esterification reaction based on this mole ratio. Moreover, although especially constraint does not have the time between measurements of a slurry consistency, measured value for 5 - 15 minutes is moving-average-deviation-ized preferably, and computing the mole ratio of EG/TPA continuously and controlling it can control most stably.
[0013] Especially a class will not be limited if the liquid density meter used by this invention is an online type which does not check the flow of a slurry. There are an oscillating type adapting the resonant frequency of oscillating tubing or diaphram being in inverse proportion as a liquid density meter generally known according to measurement fluid density change, and changing, an optical refraction type adapting the total reflection angle of light changing with the measurement fluid density of a passage way, a radiation type adapting the attenuation factor of a gamma ray, etc., and especially an oscillating type with a wide measuring range with the sufficient accuracy of measurement is desirable.
[0014] To make about 500mm into the shape of a straight pipe before and after density meter equipment preferably, to consider as a facility which passes constant flow that effect of the rate of flow of a liquid should be made the minimum, that it is the structure which makes effect to a pressure and temperature small as much as possible, and to be the structure which makes surrounding vibration the minimum further are desired so that it may have the passage which pours a liquid by rectification as a important matter on the structure of a liquid density meter. moreover, the need measuring range -- usually -- 600 - 1600 kg/m3 -- desirable -- 1300 - 1350 kg/m3 it is -- the need accuracy of measurement -- usually -- 0.8 kg/m3 the above -- desirable -- 0.5 kg/m3 It is above.

[0015] Adjustment of accommodation of the speed of supply of the ethylene glycol to the slurry tub for preparing the slurry which especially limitation does not have a means to control an esterification reaction based on the EG/TPA mole ratio called for from measurement of a slurry consistency above, and consists of a reaction band, or TPA and EG, reaction temperature, and reaction pressure etc. is attained independent or by combining. Among these, as the desirable control approach, it carries out especially by adjusting the amount of supply of EG in the preparation process of the slurry which

consists of TPA and EG. In a slurry tub, in order to make the dissolution of a TPA particle enough, a slurry is usually prepared from ordinary temperature under stirring mixing in a 100-degree C temperature requirement. It is good at a flow meter common as the detection approach of the amount of supply of EG, and an oval flow meter or a micro motion flow meter is preferably good.
[0016] In addition, in the case of a multistage reaction, EG may usually supply the whole quantity to the 1st reactor as a slurry with TPA, but it is made to carry out division supply at each reactor, and each speed of supply of EG may be adjusted. For example, a reactor is divided into two steps, and while supplying the slurry which uses EG and TPA as a principal component at the 1st reactor, nothing and the method of adjusting the speed of supply of EG of separate attachment are illustrated so that division supply of the EG may be carried out independently at the 2nd reactor.
[0017]
[Example] Hereafter, although an example explains this invention, this invention is not limited to an example, unless the summary is exceeded.
[0018] Continuation supply was carried out by 3.4 Ton/Hr, and the slurry which the mole ratio of EG/TPA becomes from a target 1.51 by the system of reaction like example 1 drawing 1 at the 1st-step esterification reaction vessel was made to react with the reaction temperature of 260 degrees C, and reaction pressure 1.5 atmospheric pressure (85.0% of target esterification conversion). Next, the BHET slurry generated by the 1st step reaction vessel was supplied to the 2nd-step esterification reaction vessel by 2.6 Ton/Hr, and EG was supplied by 150 kg/H, and it was made to react with the reaction temperature of 260 degrees C, and reaction pressure 1.05 atmospheric pressure (95.0% of target esterification conversion).
[0019] In the above, the slurry consistency was measured with the oscillating-type density meter (the product made from Solartron Transducers, Type7840 liquid density meter), and EG amount of supply was controlled so that measured value for 10 minutes was moving-average-deviation-ized and this calculation value became 1343 kg/m3 (slurry mole ratio 1.51). In addition, esterification conversion sampled the reactant with four time intervals, measured the acid number and the Ken **, and asked for them from the following formula.
[0020]
[Equation 1]

$$\text{エステル化反応率（%）} = \frac{\text{ケン価} - \text{酸価}}{\text{ケン価}} \times 100$$

The esterification conversion of step [2nd] after changed [the mole ratio of EG/TPA of the place which carried out continuous running of the above for five days, and a supply slurry / the esterification conversion of 1.51**0.01 and step / 1st / after] at 95.0**0.3% 85.0**0.5%.
[0021] The esterification conversion of 1.51**0.03 and step [1st] after was [esterification conversion of step / 2nd / after of mole ratio of EG/TPA of place / which was performed like example 1 except having not performed control by example of comparison 1 density meter / and supply slurry] 95.0**0.5% 85.0**1.0%.
[0022]
[Effect of the Invention] By becoming controllable [the EG/TPA mole ratio in a slurry] by this invention, and avoiding fluctuation of the esterification conversion resulting from the mole-ratio fluctuation which was a problem conventionally, a setup of the following polycondensation reaction condition serves as ****, and the quality of a product polymer improves as a result.

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CLAIMS

[Claim(s)]
[Claim 1] The continuation esterification approach of the terephthalic acid characterized by detecting continuously the mole ratio of ethylene glycol to the terephthalic acid in a slurry, and controlling an esterification reaction based on this mole ratio by making it face to supply the slurry which uses a terephthalic acid and ethylene glycol as a principal component to a reaction band, and to esterify continuously, installing a liquid density meter in the slurry supply way to a reaction band, and measuring a slurry consistency.
[Claim 2] Supply a terephthalic acid and ethylene glycol to a slurry tub, and it makes it face the obtained slurry to supply a reaction band and to esterify continuously. By installing a liquid density meter in the slurry supply way to a reaction band, and measuring a slurry consistency The continuation esterification approach of the terephthalic acid characterized by controlling an esterification reaction by detecting continuously the mole ratio of ethylene glycol to the terephthalic acid in a slurry, and adjusting the speed of supply of the ethylene glycol to a slurry tub based on this mole ratio.
[Claim 3] The continuation esterification approach of the terephthalic acid of claim 1 characterized by adjusting the speed of supply of the ethylene glycol of nothing and separate attachment so that division supply of the ethylene glycol may be carried out independently in the 2nd reaction band while dividing an esterification reaction zone region into two steps and supplying the slurry which uses ethylene glycol and a terephthalic acid as a principal component to the 1st reaction band.

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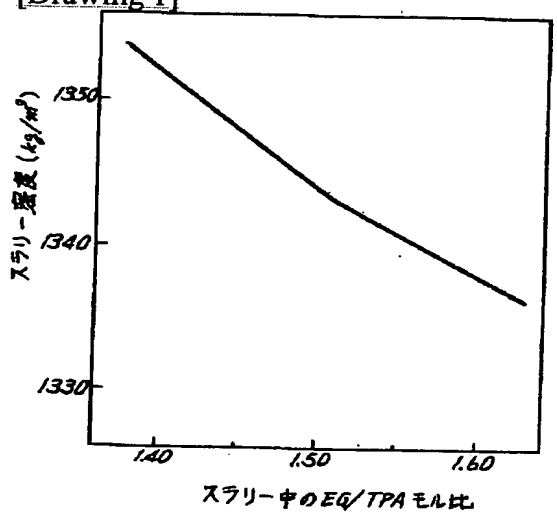
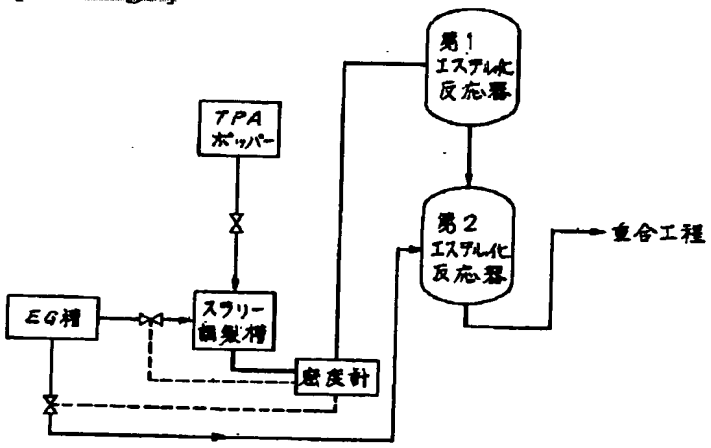
DRAWINGS

[Drawing 1]



[Drawing 2]



[Translation done.]